(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 352 849
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 89201908.4

(51) Int. Cl.[4]: C07D 301/10 , //B01J23/68

(22) Date of filing: 19.07.89

(30) Priority: 25.07.88 US 224049

(43) Date of publication of application:
31.01.90 Bulletin 90/05

(84) Designated Contracting States:
BE DE ES FR GB IT NL SE

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(54) **Process for starting-up an ethylene oxide reactor.**

(57) This invention relates to a process for starting up a fixed bed ethylene oxide reactor containing a catalyst comprising silver, an alkali metal promoter and a rhenium co-promoter supported on an alumina carrier, which process comprises:

a) heating the reactor to a temperature within 5 °C to 55 °C below the normal operating conditions,

b) passing an ethylene-containing gas over the catalyst in the reactor at a flow rate between 5 to 40 percent of the design flow rate,

c) adding a chlorohydrocarbon moderator to the gas passing over the catalyst and after between 0.1 to 10 millilitres of moderator (basis liquid) per 28.3 litres of catalyst has been added,

d) adding oxygen to the gas passing over catalyst, and raising the reactor temperature and gas flow rates to operating conditions.

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PROCESS FOR STARTING-UP AN ETHYLENE OXIDE REACTOR

This invention relates to a process for starting-up a fixed bed ethylene oxide reactor containing a catalyst comprising silver, alkali metal promoter and rhenium co-promoter supported on an alumina carrier.

A number of commercial ethylene oxide processes utilize a tube sheet reactor for converting ethylene to ethylene oxide. This fixed bed reactor typically utilizes a silver-based catalyst which has been supported on a porous support and which is typically promoted with an alkali metal promoter. The shell side of the ethylene oxide reactor typically utilizes a high temperature coolant to remove the heat generated by the oxidation reaction. Under operating conditions a chlorohydrocarbon moderator is utilized to control the oxidation reaction.

The usual practice for starting up new silver-based ethylene oxide catalysts in a commercial plant is to first add ethylene and diluent gas, then slowly introduce oxygen to get the reaction started, then to gradually introduce chlorohydrocarbon moderator to control the reaction after it is producing enough heat to become self-sustaining. For the traditional silver-based, alkali metal promoted supported catalyst, the chlorohydrocarbon moderator serves to decrease the activity (i.e., raise the temperature required to obtain a given conversion level) while increasing selectivity to ethylene oxide. When utilizing conventional alkali-promoted, supported silver catalysts, the catalysts are very active at normal start-up temperatures. Chlorohydrocarbon moderator levels are introduced after start-up to control the high catalyst activity to reduce the conversion level, and to prevent a "run away".

This invention relates to a process for starting up a fixed bed ethylene oxide reactor containing a catalyst comprising silver, an alkali metal promoter and a rhenium co-promoter supported on an alumina carrier, which process comprises:

a) heating the reactor to a temperature within 5 °C to 55 °C below the normal operating conditions,

b) passing an ethylene-containing gas over the catalyst in the reactor at a flow rate between 5 to 40 percent of the design flow rate,

c) adding a chlorohydrocarbon moderator to the gas passing over the catalyst and after between 0.1 to 10 millilitres of moderator (basis liquid) per 28.3 litres of catalyst has been added,

d) adding oxygen to the gas passing over catalyst, and raising the reactor temperature and gas flow rates to operating conditions.

This process is applied to new or fresh catalysts, as well as to used catalysts that have been subjected to a prolonged shut-down period.

The catalyst that is used in the fixed bed reactor that is started up by the process of the instant invention comprises silver, alkali metal promoter and rhenium co-promoter supported on an alumina carrier preferably an alpha-alumina carrier. Other moderators and promoters may be utilized but the key to the instant invention is the use of a catalyst containing the rhenium as a promoter.

The catalysts used in the instant process comprise a catalytically effective amount of silver, a promoting amount of alkali metal and a promoting amount of rhenium. Preferably the major amount of alkali metal promoter present is a higher alkali metal selected from potassium, rubidium, cesium and mixtures thereof. Most preferably the alkali metal is cesium. Combinations of alkali metals, such as cesium and lithium are quite suitable. Concentrations of alkali metal (measured as the metal) between 10 and 3000 ppm, preferably between 15 and 2000 ppm and more preferably between 20 and 1500 ppm by weight of total catalyst are desirable. The rhenium promoter concentration will range from 0.1 to 10, preferably from 0.2 to 5 millimoles, measured as the element, per kilogram of total catalyst. Other co-promoters may be present. Desired co-promoters are selected from compounds of sulfur, molybdenum, tungsten, chromium and mixtures thereof. Particularly preferred as a co-promoter is sulfate. Co-promoter concentrations will range from 0.1 to 10, preferably from 0.2 to 5 millimoles, measured as the element, per kilogram of total catalyst.

The process of the instant invention is applied to new catalysts as well as to aged catalysts that, due to a plant shut-down, have been subjected to a prolonged shut-in period.

When new catalysts are utilized it has been found useful to subject these catalysts to a high temperature with nitrogen gas passing over the catalyst. The high temperature converts a significant portion of the organic nitrogen compounds used in the manufacture of the catalyst to nitrogen-containing gases which are swept up in the nitrogen stream and removed from the catalyst. Typically, the catalyst is loaded into the tube reactor and by utilizing a coolant heater, the temperature of the reactor is brought up to within 5 °C to 55 °C, preferably to within 11 °C to 28 °C below the normal operating conditions. Temperatures closer to the normal operating temperatures can be utilized, but in most commercial operations the coolant heater is not sized large enough to bring the reactor up to full operating temperatures. In general, the reactor is heated to a temperature between about 204 °C and 247 °C. A nitrogen flow,

if utilized, is then passed over the catalyst at a flow rate typically between 5 to 40% of the design flow rate, preferably between 15 and 25% of the design flow rate. The nitrogen flow may be initiated before reactor heatup, during reactor heatup or after the reactor has reached the desired temperature. The nitrogen gas is typically passed over the catalyst for a period of time ranging from $\frac{1}{2}$ of a day to 7 days. During this purge time the nitrogen stream is monitored for nitrogen-containing decomposition products from the catalysts. The startup of used catalysts may or may not require the use of nitrogen, but it is frequently used. When nitrogen is not utilized, the reactor may be pressurized with ethylene, methane or other non-oxidizing gas.

After the nitrogen-containing decomposition products have been removed to a suitable low level, generally less than about 10 ppm, the recycle loop to the ethylene oxide reactor is then pressurized with ethylene and a suitable ballast gas such as methane in preparation for a start up. A gas flow rate of between 5 to 40% of design rate, preferably from 15 to 25% of design rate is maintained over the reactor.

A chlorohydrocarbon moderator is then added to the recycle gas stream being fed to the ethylene oxide reactor. The amount of chlorohydrocarbon moderator is added slowly over a period of several hours until approximately 0.1 to 10 cubic centimeters (millilitres), preferably 0.5 to 5, and more preferably 0.75 to 2 cubic centimeters (millilitres) of chlorohydrocarbon moderator (basis liquid) per cubic foot (28.3 litres) of catalyst in the reactor bed has been added to the recycle feed loop. When fresh catalyst is used, it contains no chloride on its silver surfaces and hence the initial chlorohydrocarbon that is added to the recycle feed stream will be absorbed by the catalyst until the catalyst reaches a steady state at which point the chlorohydrocarbon moderator will begin to build up in the recycle feed stream to a steady state level. Suitable chlorohydrocarbons used as moderators comprise the C_1 to C_8 chlorohydrocarbons, that is compounds comprising hydrogen, carbon and chlorine. Preferably these chlorohydrocarbons are C_1 to C_4 chlorohydrocarbons and most preferably they are C_1 and C_2 chlorohydrocarbons. The chlorohydrocarbons may be optionally substituted with fluorine. Illustrative examples of these moderators include methyl chloride, ethyl chloride, ethylene dichloride, vinyl chloride or mixtures thereof. Preferred moderators are ethyl chloride, ethylene dichloride and vinyl chloride, particularly ethyl chloride. The moderator is added to the reactor during this step preferably during a period of time ranging from 2 to 6 hours. These times, however, are not critical and shorter or longer periods can be used.

After the chlorohydrocarbon moderator has been fed to the catalyst in the above-defined range, oxygen is then added to the recycle feed stream at initially from 5 to 40% of design rate, preferably from 15 to 25% of design rate. Reaction initiation will occur within a few minutes of the addition of the oxygen, after which point the oxygen feed to the reactor, the feed gas to the reactor and the reactor temperature are raised to approximately the design conditions over a period of time ranging from 15 min to 6 h, preferably from 30 min to 4 h.

The ranges and limitations provided in the instant specification and claims are those which are believed to particularly point out and distinctly claim the instant invention. It is, however, understood that other ranges and limitations that perform substantially the same function in substantially the same manner to obtain the same or substantially the same result are intended to be within the scope of the instant invention as defined by the instant specification and claims.

The following example is provided as a means to illustrate the process of the instant invention and is not to be construed as limiting the invention.

Example

An alumina supported silver catalyst containing as promoters cesium, lithium, rhenium and sulfate was loaded into a fixed bed tubular ethylene oxide reactor. The reactor was heated to about 221 °C utilizing the reactant coolant heaters during which nitrogen gas was circulated through the reactor at about 25% of design flow rate. Nitrogen flow was continued for about 24 h, at which point the flow was stopped. The reactor was checked for ammonia gas, which is a decomposition product of some of the organonitrogen compounds used in preparing the catalyst, and it was found that ammonia was less than about 5 ppm. Pressurization of the reactor recycle loop reactor with ethylene and methane in preparation for start up was initiated. A gas flow rate of about 20% of design flow rate was maintained to the reactor.

Ethyl chloride was then added to the gas stream flowing over the catalyst. The ethyl chloride target flow rate to the reactor was about 400 ml per h. The total dosage applied to the catalyst in the reactor prior to oxygen addition was about 1.3 ml of liquid ethyl chloride per 28.3 litres of catalyst.

At about 3 h and 45 min after the start of the ethyl chloride addition, oxygen was then added at about 17% of design flow rate at a coolant temperature now of about 232 °C. Reaction initiated within 2 min of oxygen addition with about 1% oxygen in the feed. The oxygen flow rate was quickly increased to about 70% of design flow rate

during the first 20 min after start up. During this period the feed gas flow was increased from 25% to about the maximum. Maximum catalyst temperature to this point was about 274 °C. After about 1 h after oxygen initiation, the reactor coolant temperature reached about 250 °C. Minor adjustments to the reactor conditions were made over the next several days to bring the catalyst to its optimum operating conditions.

Claims

1. A process for starting up a fixed bed ethylene oxide reactor containing a catalyst comprising silver, an alkali metal promoter and a rhenium co-promoter supported on an alumina carrier, which process comprises:

a) heating the reactor to a temperature within 5 °C to 55 °C below the normal operating conditions,

b) passing an ethylene-containing gas over the catalyst in the reactor at a flow rate between 5 to 40 percent of the design flow rate,

c) adding a chlorohydrocarbon moderator to the gas passing over the catalyst and after between 0.1 to 10 millilitres of moderator (basis liquid) per 28.3 litres of catalyst has been added,

d) adding oxygen to the gas passing over catalyst, and raising the reactor temperature and gas flow rates to operating conditions.

2. A process as claimed in claim 1 wherein in step b) the ethylene-containing gas is passed over the reactor at a flow rate between 15 to 25 percent of the design flow rate.

3. A process as claimed in claim 1 or 2 wherein in step b) the ethylene-containing gas also contains nitrogen and methane.

4. A process as claimed in one or more of the claims 1-3 wherein the chlorohydrocarbon moderator is a C_1 to C_8 chlorohydrocarbon.

5. A process as claimed in claim 4 wherein the chlorohydrocarbon moderator is a C_1 to C_4 chlorohydrocarbon.

6. A process as claimed in claim 5 wherein the chlorohydrocarbon moderator is a C_1 or C_2 chlorohydrocarbon.

7. A process as claimed in claim 6 wherein the chlorohydrocarbon moderator is methyl chloride, ethyl chloride, ethylene dichloride or vinyl chloride or mixtures thereof.

8. A process as claimed in claim 1 wherein in step c) from 0.5 to 5 millilitres of moderator per 28.3 litre of catalyst is added.

9. A process as claimed in claim 8 wherein in step c) from 0.75 to 2 millilitres of moderator per 28.3 litre of catalyst has been added.

10. A process as claimed in claim 8 or 9 wherein in step c) the moderator is added over a period of time ranging from 1 to 10 hours.

11. A process as claimed in claim 10 wherein in step c) the moderator is added over a period of time ranging from 2 to 6 hours.

12. A process as claimed in claim 1 wherein in step d) the reactor temperature and gas flow rates are raised to operating conditions over a period of time after the start of the oxygen addition ranging from 15 minutes to 6 hours.

13. A process as claimed in one or more of the claims 1-12 wherein nitrogen gas is passed over the catalyst prior to passing ethylene-containing gas of step b) over the catalyst.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 89201908.4

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	EP - A2/A3 - 0 244 895 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) * Abstract * --	1	C 07 D 301/10 //B 01 J 23/68
A	EP - A2/A3 - 0 168 782 (HOECHST AKTIENGESELLSCHAFT) * Claim 1 * --	1	
A	EP - A1 - 0 226 234 (THE DOW CHEMICAL COMPANY) * Claim 1 * ----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 07 D 301/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	06-10-1989	BRUS

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document